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(71) Applicant(s)

Avecia B.V.
(Incorporated in the Netherlands)
PO Box 123, Sluisweg 12, 5140 AC Waalwijk,
Netherlands

(72) Inventor(s)

Geradus Cornelis Overbeek
Rajasingham Satgurunathan
Johannes Ludovicus Martinus Van Hilst
Johannes Marinus Geurts

(74) Agent and/or Address for Service

Maja Schmitt
Avecia Limited, PO Box 42, Hexagon House, Blackley,
MANCHESTER, M9 8ZS, United Kingdom

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(54) Abstract Title

Aqueous multi-polymer dispersion

(57) Solvent-free aqueous multipolymer dispersion comprising (A) a soft acrylic polymer(s), (B) a hard acrylic polymer(s), where the Tg difference between the (A) and (B) polymers is $\geq 30^{\circ}\text{C}$, and (C) a chain-extended polyurethane whose prepolymer has an acid value of ≤ 35 mg KOH/g and which has less than 0.2 mole per gram of olefinically unsaturated bonds.

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AQUEOUS MULTIPOLYMER DISPERSIONS

The present invention relates to aqueous multipolymer dispersions comprising at least two acrylic polymers with certain Tg characteristics and a certain polyurethane.

5 It is known in the art to employ aqueous polymer dispersions of acrylic polymers or, alternatively, of polyurethanes as the basis of aqueous compositions for the production of coatings, the acrylic polymer or polyurethane providing the binder material for such coatings. It is further known to employ acrylic polymers and polyurethanes in combination in aqueous polymer dispersions in order to further upgrade the properties of the resulting
10 coating whereby the presence of each type of polymer (acrylic or urethane) will ameliorate certain properties of the coating in comparison to using the other type of polymer on its own.

We have now discovered that a certain combination of acrylic polymers and polyurethane in aqueous dispersion results in exceptionally good properties, and in
15 particular a very advantageous balance of minimum film forming temperature (MFFT) and properties such as block resistance, early blocking, and hardness, which are normally dependent on the glass transition temperature Tg of the polymer binder, whereby one can obtain, without the requirement of a coalescent solvent, low MFFT, resulting in facile film formation, in conjunction with high hardness, good block resistance and good early
20 blocking resistance. This is surprising because the achievement of low MFFT and properties such as high hardness and good block resistance would normally work against each other (e.g. if the aqueous dispersion, or aqueous composition containing it, has a low MFFT - which normally corresponds with a low polymer Tg, it will not tend to yield particularly high hardness or good block resistance in the resulting coating - such
25 properties being known to improve with increasing Tg other things being equal). Normally, if one used a polymer dispersion resulting in high hardness and good block resistance, it would be necessary to incorporate a coalescent solvent to achieve low MFFT, which use, however, is itself undesirable for environmental and flammability reasons. The invention dispersion surprisingly overcomes such drawbacks.

30 According to the present invention there is provided an aqueous multipolymer dispersion which is substantially solvent-free and comprises the following polymers:

- (A) an acrylic polymer(s) having a Tg of less than 20°C;
- (B) an acrylic polymer(s) having a Tg of at least 20°C;
wherein the Tg of polymer(s) of (B) is at least 30°C higher than the Tg of the
35 polymer(s) of (A), preferably at least 50°C higher;
- (C) a polyurethane polymer(s) which is a chain-extended product formed from reactants which comprise:

(1) an aqueous-dispersed isocyanate-terminated prepolymer having an acid value of ≤ 35 mgKOH/g of prepolymer (solids), preferably ≤ 30 mgKOH/g, and being formed from reactants which comprise:

(i) at least one organic polyisocyanate,

(ii) an organic isocyanate-reactive component comprising at least one polymeric polyol, and

(2) an active hydrogen chain-extending compound(s);

wherein said polyurethane polymer has less than 0.2 mmole per gram of olefinically unsaturated bonds.

There is further provided according to the invention a substantially solvent-free aqueous coating composition comprising an aqueous multipolymer dispersion as defined above.

There is further provided according to the invention a method of coating a substrate using an aqueous dispersion or aqueous composition as defined above.

There is further provided according to the invention a coating obtainable or derived from an aqueous dispersion or aqueous dispersion as defined above.

There is further provided according to the invention a substrate having a coating obtainable or derived from an aqueous dispersion or composition as defined above.

By a substantially solvent-free aqueous dispersion, or aqueous composition comprising it, is meant that the dispersion or composition must contain less than 1.5 wt % of organic solvent(s) based on total polymer solids, more preferably less than 0.5 wt %, and most preferably no solvent at all. It is particularly preferred that the aqueous dispersion or composition contains less than 5 wt % of organic solvent(s) based on polyurethane solids, more preferably less 2 wt %, and most preferably no solvent at all. (In this specification organic plasticisers are intended to be within the scope of the term "solvent"; these, like coalescent solvents, are also used in the art to decrease MFFT although strictly speaking they are not solvents).

Accordingly, for the purposes of the invention an "aqueous dispersion" of a polymer, or an "aqueous composition" comprising it, means a dispersion or composition of the polymer in a liquid carrier medium of which water is the principle or only component - consistent with such a dispersion or composition being substantially solvent-free as defined above. The invention dispersion will typically comprise colloidally dispersed particles of acrylic and polyurethane particles, i.e. will typically be in the form of an aqueous polymer latex.

An acrylic polymer(s) of the invention dispersion having Tg of less than 20°C is termed herein a "soft" polymer for convenience, while an acrylic polymer(s) of the invention dispersion having Tg of at least 20°C is termed herein a "hard" polymer for convenience. Preferably a soft acrylic polymer has a Tg within the range of from -70 to

19°C, more preferably from -35 to 15°C and most preferably from -15 to 10°C, and a hard acrylic polymer preferably has a T_g within the range of from 40 to 115°C, more preferably 60 to 115°C, and most preferably from 70 to 95°C. The T_g of a hard polymer(s) (B) should be at least 30°C, higher than the T_g of a soft polymer(s) (A), more preferably at least 50°C, and most preferably at least 65°C. The weight ratio of soft to hard acrylic polymers is preferably within the range of from 30/70 to 90/10, more preferably from 40/60 to 85/15, and most preferably from 45/55 to 80/20.

It is within the scope of the invention for the polyurethane polymer(s) by itself to be film forming at ambient temperature (ambient temperature being taken herein as 10 to 25°C) or non film forming at ambient temperature. By this is meant that the polyurethane polymer(s) if applied on its own as an aqueous dispersion having a solvent content which would correspond to a substantially solvent-free aqueous dispersion in the invention composition (i.e. when combined with the acrylic polymers) as defined supra can be film forming at ambient temperature or non film forming at ambient temperature as the case may be.

In one embodiment of the invention, the polyurethane polymer(s) by itself is film forming at ambient temperature, the weight ratio of the soft to hard acrylic polymers is within the range of from 30/70 to 50/50, and the combined amount of the film forming polyurethane polymer(s) and the soft acrylic polymer(s) corresponds to at least 45 weight % of the total amount of the polymer(s) of (A), (B) and (C), more preferably at least 50 weight %.

In another embodiment of the invention, the polyurethane polymer by itself is non film forming at ambient temperature, the weight ratio of the soft to hard acrylic polymers is within the range of from more than 50/50 to 90/10, and the combined amount of the non-film forming polyurethane polymer(s) and the hard acrylic polymer(s) is less than 55 weight % of the total amount of the polymers of (A), (B) and (C), more preferably less than 50 weight %.

The acrylic polymers of differing T_g (as defined) may be present in the dispersion as a single blend of preformed (separately prepared) polymers, or as a sequentially-formed composition of the polymers, whereby one acrylic polymer has been prepared (by polymerisation of its constituent monomers) in the presence of another, preformed, acrylic polymer (possibly, but not necessarily, resulting in the acrylic polymers being in a core/shell particle arrangement), again so that there is a T_g difference (as defined) between the acrylic polymers.

In a further possibility, an acrylic polymer(s) is present in the dispersion as a polyurethane/acrylic polymer hybrid (hereinafter a u/a hybrid) by which is meant in this specification that the acrylic polymer(s) has been prepared in-situ in the presence of the polyurethane polymer during and/or after the latter's formation, whereby the monomer(s) for the acrylic polymer(s) i.e. tends to swell (i.e. become absorbed in) the polyurethane

particles, resulting in a hybrid of the urethane and acrylic polymers(s) in which at least part of the acrylic polymer(s) (and usually most or all of the acrylic polymer(s)) is located within and/or as part of the polyurethane particles. [It should be appreciated, that the polymerisation of the monomer(s) to form the acrylic part of the u/a hybrid may be done in such a way as to produce only one acrylic polymer with a single Tg, or 2 or more acrylic polymers with differing Tg's]. The acrylic polymer(s) of the u/a hybrid may then be combined with a further acrylic polymer(s) to provide the soft and hard acrylic polymers of the invention dispersion (although it is also possible in principle for all the soft and hard acrylic polymers to be provided by the u/a hybrid alone). For example, the u/a hybrid may be mixed with one or two separately prepared acrylic polymers, or with a sequentially formed pair of acrylic polymers (see above), or all three types of acrylic polymer location may be present. In all cases, of course, the acrylic polymers must be of such Tg's so as to provide a Tg difference as defined. Examples of the various types of polymer systems available will be discussed in more detail later in this specification.

The polyurethane polymer(s) of the invention dispersion more preferably has less than 0.1 mmole per gram of olefinically unsaturated bonds, and most preferably 0 mmoles per gram of olefinically unsaturated bonds (i.e. no olefinically unsaturated bonds at all).

The polyurethane polymer(s) of the invention dispersion preferably has internal dispersing groups built into its structure (preferably in pendant and/or terminal positions) during its synthesis (usually as part of the prepolymer) whereby such groups preferably render the polyurethane self-water-dispersible. Thus, although the polyurethane may in principle be dispersible in water to form a stabilised dispersion therein solely as a result of the use of an external surfactant(s) (if the polyurethane polymer has no internal dispersing groups), it is far more preferably dispersible as a result of the presence of internal dispersing groups - optionally, or if necessary, in conjunction with an external surfactant(s). If a polyurethane polymer containing internal dispersing groups forms a stable dispersion in water without the requirement for added (i.e. external) surfactant(s) it is herein termed self-water-dispersible, although when forming an aqueous dispersion of such a polymer, external surfactant(s) may optionally still be employed if desired. Such internal dispersing groups are more usually chain pendant groups and may be of the ionic type (viz anionic or cationic) or of the nonionic type, or a combination of ionic and nonionic types of group. For example, where the dispersing groups are of the anionic type, such as carboxyl groups, which need to be in their neutralised form (such as carboxylate anionic groups) to effect their internal dispersing action, the required amount of dispersing groups could be achieved by neutralising only a certain proportion of the potential anionic groups (e.g. carboxyl groups) or alternatively, fully neutralising all such groups but having a lower amount of them in the polymer.

The organic polyisocyanate(s) (1)(i) used for making the prepolymer of the polyurethane is preferably an organic diisocyanate(s). Such organic diisocyanate(s) may

be an aliphatic (which term includes cycloaliphatic), araliphatic or aromatic polyisocyanate. Preferably, however, the polyisocyanate(s) is aliphatic.

Examples of suitable aliphatic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, cyclopentylene diisocyanate, p-tetra-methylxylene diisocyanate (p-TMXDI) and its meta isomer (m-TMXDI), hydrogenated 2,4-toluene diisocyanate, hydrogenated 2,6-toluene diisocyanate, and 1-isocyanato-1-methyl-3(4)-isocyanatomethyl-cyclohexane (IMCI).

Suitable non-aliphatic polyisocyanates include p-xylylene diisocyanate, 1-4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-diphenylmethane diisocyanate, and 1,5-naphthylene diisocyanate.

Mixtures of polyisocyanates can be used and also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred polyisocyanates are 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate and TMXDI (p or m).

The polymeric polyol(s) of the isocyanate-reactive component (1)(ii) is preferably a polymeric diol, but may be or include polymeric polyol(s) of functionality more than 2. The polymeric polyol(s) preferably has a number average molecular weight (hereinafter M_n) within the range of from 500 to 8,000 g/mole, more preferably from 700 to 3,000 g/mole. Such polyol(s) is preferably essentially linear. Such polyol(s) in principle may be selected from any of the chemical classes of polymeric polyols used or proposed to be used in polyurethane synthesis. In particular the polymeric polyol(s) may be a polyester polyol, a polyesteramide polyol, a polyether polyol, a polythioether polyol, a polycarbonate polyol, a polyacetal polyol, a polyolefine polyol or a polysiloxane polyol. More preferably the polymeric polyol(s) is selected from a polyester polyol, a polyether polyol, a polysiloxane polyol, and particularly preferably a polyether polyol and a polyester polyol.

Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, furan dimethanol, cyclohexane dimethanol, glycerol, trimethylolpropane or pentaerythritol, or mixtures thereof, with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their methyl esters, phthalic anhydrides or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a polyol may also be used. Polyesteramides may be obtained by the inclusion of amino-alcohols such as ethanolamine in polyesterification mixtures.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide or tetrahydrofuran or by the addition of one or more such oxides to polyfunctional initiators, for example water, methylene glycol, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylpropane, pentaerythritol or Bisphenol A. Especially useful polyether polyols include polyoxypropylene diols and triols, poly (oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to appropriate initiators and polytetramethylene ether glycols obtained by the polymerisation of tetrahydrofuran.

Polyols having Mn below 500 (which may be polymeric, or rather oligomeric, or monomeric) may optionally be used as part of the isocyanate-reactive component (1)(ii) in the preparation of the isocyanate-terminated prepolymer. Examples particularly include diols and (less preferably) triols or tetrols and mixtures thereof. Examples of such lower molecular weight polyols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, 1,4-cyclohexane dimethanol, furan dimethanol, glycerol and the reaction products, up to Mn 499, of such polyols with propylene and/or ethylene oxide.

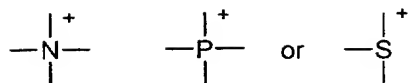
The isocyanate-reactive component may also include an organic monool(s).

It will be appreciated that the isocyanate-reactive component (1)(ii) may optionally include an isocyanate-reactive compound(s) which is other than a polyol (e.g. a diamine or an aminoalcohol); however the polyol component will normally be entirely of substantially comprised of polyol reactant(s).

As discussed supra the polyurethane polymer(s) of the present invention is preferably self-water-dispersible, by which is meant that it preferably forms stable dispersions in water without the requirement for added (i.e. external) surfactant(s), although these can be present if desired. Such preferred self-water-dispersibility of the polyurethane arises from the presence of internal dispersing groups built into the polymer during its synthesis (as discussed supra). As mentioned above such groups may be of the ionic (anionic or cationic) or nonionic type and may be incorporated by employing a reactant(s) bearing such groups (or in the case of anionic or cationic dispersing groups, groups which may if necessary subsequently be converted to such dispersing groups).

Such a reactant(s) may form part of the isocyanate-reactive component (1)(ii) and/or the polyisocyanate (1)(i), and/or may form part of the active hydrogen chain-extending compound(s) (2). Most preferably such a reactant(s) is part of the isocyanate-reactive component (1)(ii) and/or the polyisocyanate (1)(i) since this results in a self-water-dispersible polyurethane prepolymer component (and hence a final polyurethane polymer which is self-water-dispersible).

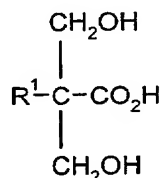
Ionic dispersing groups (as mentioned supra) may be cationic, for example



or, more preferably, anionic, for example $-\text{SO}_3^-$, $-\text{OSO}_3^-$, $-\text{PO}_3^-$, and in particular a carboxylate salt group $-\text{CO}_2^-$.

Groups which are subsequently converted to dispersing groups are particularly unionised (or substantially unionised) acid or basic groups which can be e.g. converted to corresponding anionic or cationic groups by neutralisation or quaternisation. For example free (unionised) carboxylic acid groups can be neutralised to carboxylate anionic groups while tertiary amine groups can be quaternised to quaternary ammonium groups.

It is most preferred that ionic groups are incorporated into the prepolymer (and/or less preferably by being part of the chain-extender component) via carboxylic-acid groups which are subsequently neutralised to carboxylate ion groups using agents such as a tertiary amine, examples of which include triethylamine, triethanolamine, dimethylethanolamine or N-methylmorpholine, or an alkaline hydroxide such as K, Na or Li hydroxide or a quaternary ammonium hydroxide. Ammonia itself may also be used. Examples of reactants for effecting such incorporation include carboxyl group-containing diols and triols, and in particular dihydroxy alkanedioic acids of the formula:



wherein R^1 is hydrogen or alkyl (usually 1-5C). The most preferred carboxyl-bearing polyol is 2,2-dimethylol propionic acid (DMPA). Another preferred one is 2,2-dimethylol-n-butyric acid (DMBA).

The conversion of any acid groups present in the prepolymer to anionic salt groups may be effected by neutralising the acid groups before, after or simultaneously with the formation of an aqueous dispersion of the prepolymer. Where acid groups are present additionally or only in the final polyurethane by virtue of being incorporated additionally or only during the chain extension step the conversion of such groups to anionic salt groups may be effected by neutralising these acid groups during or after the formation of the final polyurethane dispersion.

Nonionic dispersing groups are typically pendant polyoxyalkylene groups, particularly polyethylene oxide (PEO) groups. Such groups may, for example be provided by employing as a reactant in the prepolymer formation (and/or less preferably by being part of the chain-extender component) diols having pendant PEO chains such as those described in the prior art, for example US 3905929. In US 3905929 examples of such compounds are disclosed which may be obtained by reacting one mole of an organic

diisocyanate in which the two isocyanate groups have different reactivities with approximately one mole of a polyethylene glycol mono-ether and then reacting the adduct so obtained with approximately one mole of a dialkanolamine, for example diethanolamine. Chain-pendant PEO groups may also be introduced by employing certain amine and hydroxyl functional compounds, or diols, as disclosed in EP 0317258, where such compounds are obtained by oxyalkylating a defined polyether amine containing PEO residues.

If desired, the PEO chains may contain units of other alkylene oxides in addition to the ethylene oxide units. Thus, PEO chains in which up to 60% of the alkylene oxide units are propylene oxide units, the remainder being ethylene oxide units, may be used.

Nonionic dispersing groups may also be additionally or alternatively incorporated into the prepolymer by using as a reactant in the prepolymer formation poly (preferably di) isocyanates bearing pendant PEO chains (e.g. those described in US 3905929). This is not a preferred expedient however.

Generally speaking, it is preferred to use within the range of from 15 to 63 (more preferably 24 to 56, and most preferably 31 to 49) milliequivalents of ionic (preferably anionic) internal dispersing groups per 100 g of urethane prepolymer solids (assuming such groups are being employed). In the case of nonionic internal dispersing groups (such as PEO chains), it is, generally speaking, preferred to use 3 to 30 weight % (more preferably 5 to 20 weight %) of such groups based on the weight of polyurethane polymer solids in the case where no ionic internal dispersing groups are present, and 0 to 15 weight % (more preferably 0 to 10 weight %) where ionic internal dispersing groups are also present. In the case of using anionic (or cationic) dispersing groups this may be achieved by incorporating an amount of potential anionic (or cationic) groups into the polyurethane which on full neutralisation (or quaternisation) will provide the above preferred amount of ionic groups. Alternatively, an amount of potential anionic (or cationic) groups may be incorporated which on full neutralisation (or quaternisation) would provide a level greater than that preferred range mentioned above and only neutralising (or quaternising) sufficient of these groups to provide the above preferred range of ionic dispersing groups (partial neutralisation or quaternisation).

The isocyanate-terminated polyurethane prepolymer may be prepared in conventional manner by reacting a stoichiometric excess of the organic polyisocyanate(s) with the isocyanate-reactive component (and any other reactants) under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until reaction between the isocyanate groups and the isocyanate-reactive (usually all hydroxyl) groups is substantially complete. During the production of the isocyanate-terminated prepolymer the reactants are generally used in proportions corresponding to a ratio of isocyanate groups to isocyanate-reactive (usually all hydroxyl) groups from about 1.1:1 to about 6:1, preferably from about 1.5:1 to 3:1 (particularly from 1.6:1 to 2.3:1).

If desired, catalysts such as dibutyltin dilaurate or stannous octoate may be used to assist prepolymer formation. An organic solvent may optionally be added before, during or after prepolymer formation to control the viscosity provided it does not vitiate the obtaining of a solvent-free final dispersion (such solvent may thus subsequently need to be removed as far as is possible). Suitable solvents which may be used include acetone, methylethylketone, dimethylformamide, diglyme, N-methylpyrrolidone, ethyl acetate, ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol monoacetates, toluene, xylene and sterically hindered alcohols such as t-butanol and diacetone alcohol. The preferred solvents are water-miscible solvents such as N-methylpyrrolidone, acetone and dialkyl ethers of glycol acetates or mixtures of N-methylpyrrolidone and methyl ethyl ketone. In cases where an acrylic polymer(s) formed in-situ with the polyurethane polymer is to be employed (see later for this embodiment), the solvent for use in the prepolymer (if having suitable solvent characteristics) may be or may comprise (e.g. optionally in conjunction with organic solvents of the type described supra) a monomer which is subsequently polymerised as the or as part of the monomer system to form the acrylic polymer(s).

The aqueous polyurethane dispersion is prepared by forming an aqueous dispersion of the isocyanate-terminated polyurethane prepolymer and dispersing it (optionally carried in an organic solvent medium which may include or consist of a monomer(s) for acrylic polymer(s)) in an aqueous medium, preferably utilising self-dispersibility properties of the prepolymer arising from internal dispersing groups in the isocyanate-terminated prepolymer, although free surfactant(s) may additionally be employed if desired, and chain-extending the prepolymer with an active hydrogen compound(s) in the aqueous phase, the chain-extender being present in the aqueous phase during dispersion or added subsequently (i.e. chain-extension can take place during and/or after the dispersion into water in this embodiment).

The prepolymer may be dispersed in water using techniques well known in the art. Preferably, the prepolymer is added to the water with agitation or, alternatively, water may be stirred into the prepolymer component.

The active hydrogen-containing chain-extender compound(s) which may be reacted with the prepolymer component is suitably a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic diamine or polyamine (i.e. having 3 or more amine groups), or hydrazine or a substituted hydrazine, or a polyhydrazide (preferably a dihydrazide).

Water-soluble chain-extenders are preferred.

Water itself may be used as an indirect chain-extender because it will slowly convert some of the terminal isocyanate groups of the prepolymer to amino groups (via unstable carbamic acid groups) and the modified prepolymer molecules will then undergo chain extension. However, this is very slow compared to chain extension using the above

mentioned active hydrogen chain-extendors (which can be called added chain-extender compounds) which will provide the predominant chain extension reaction if used.

Examples of such added chain-extendors useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, piperazine, 2-methyl piperazine, phenylene diamine, toluylene diamine, xylylene diamine, tri (2-aminoethyl) amine, 3,3-dinitrobenzidine, 4,4'-diaminodiphenylmethane, methane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolysed products. Also materials such as hydrazine (e.g. in the form of its mono hydrate), azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, dihydrazides of dicarboxylic acids and sulphonic acids such as adipic acid dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, hydrazides made by reacting lactones with hydrazine such as gamma-hydroxylbutyric hydrazide, bis-semi-carbazide, and bis-hydrazide carbonic esters of glycols. Another suitable class of chain-extendors is the so-called "Jeffamine" compounds with a functionality of 2 or 3 (available from Huntsman). These are PPO or PEO-based di or triamines, e.g. "Jeffamine" T403 and "Jeffamine" D-400.

Preferably the active hydrogen chain-extender component is or includes hydrazine (usually in the form of its monohydrate), or a di or triamine (usually a diamine) of Mn below 300.

When the chain-extender is an added component, i.e. is other than modified prepolymer molecules formed by reaction with water, for example a polyamine or diamine or hydrazine, it may for example be added to the aqueous dispersion of prepolymer, or it may for example already be present in the aqueous medium when the prepolymer is dispersed therein, or it may for example simply be fed with prepolymer to water.

The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5°C to 90°C, more preferably from 10 to 60°C.

The total amount of chain-extender material(s) employed (other than water) is preferably such that the ratio of active hydrogens in the chain-extender(s) to NCO groups in the prepolymer component is preferably within the range of from 0.7/1 to 2.0/1 more preferably 0.85/1 to 1.2/1. Of course, when water is employed as an indirect chain-extender, these ratios will not be applicable since the water, functioning both as an indirect chain-extender and a dispersing medium, will be present in a gross excess relative to the residual NCO groups.

[It is evident from all the foregoing that the term "polyurethane" as used in this specification is intended to apply not only to polymers (or prepolymers) having only urethane linkages formed from isocyanate and hydroxyl groups, but also to polymers,

prepolymers or polymer segments having, in addition to urethane linkages, linkages formed from isocyanate groups and groups such as -NH₂, -NH-, or -SH groups].

When making a u/a hybrid (as discussed earlier), monomer(s) for making the in-situ prepared acrylic polymer(s) may be introduced in the process at any suitable stage.

5 For example, when the aqueous dispersion of the urethane prepolymer is formed in the process to make the polyurethane polymer all of the monomer(s) for the acrylic polymer(s) may be added to the prepolymer prior to its dispersion into water, or all of the monomer(s) may be added subsequent to dispersion (or may have already been added to the water prior to the dispersion of the prepolymer therein), or part of the monomer(s) may be added to the prepolymer prior to dispersion and the remainder added subsequent to dispersion. In the case where all or part of the monomer(s) is added to the prepolymer prior to dispersion into water, such monomer(s) could be added to the prepolymer subsequent to its formation or prior to its formation, or some could be added subsequent to its formation and some added prior to its formation. In the case where any monomer(s) is added prior to the prepolymer formation it may (as mentioned above) provide at least part of a solvent system for the reaction to form the prepolymer (if it possesses suitable solvent characteristics).

20 The in-situ formed acrylic polymer(s) is made by an aqueous free-radical polymerisation process and such polymerisation may be performed simultaneously with the chain extension step, or performed subsequent to the chain extension step, or performed partly simultaneously with the chain extension step and partly subsequent to the chain extension step.

25 All of the monomer(s) (for an acrylic polymer) to be polymerised in a u/a hybrid may be present at the commencement of the polymerisation, or in cases where all or part of the monomer(s) to be polymerised has been introduced subsequent to the formation of an aqueous prepolymer dispersion, some or all of that monomer(s) may be added to the reaction medium during the course of the polymerisation (in one or more stages or continuously). Alternatively some or all of the monomer can be converted to polymer and be present in the aqueous phase before dispersion of the urethane prepolymer in the aqueous phase. It is to be understood (as mentioned above) that a single acrylic polymer (with one T_g) may be produced in a u/a hybrid, or 2 or more acrylic polymers may be formed with differing T_g's.

30 When a u/a hybrid is being employed in the invention dispersion, it is preferred that the weight ratio of the polyurethane polymer to the acrylic polymer(s) in the hybrid is within the range of from 5/95 to 99/1 more preferably from 15/85 to 90/10, and most preferably from 30/70 to 80/20.

The weight average molecular weight (M_w) of the polyurethane is preferably at least 10,000 g/mole more preferably at least 25,000 g/mole and most preferably at least 40,000 g/mole. The M_w normally does not usually exceed 1,500,000 g/mole.

Turning now generally to the production of an acrylic polymer for use in the invention dispersion, whether for use in a simple blend, or as each polymer component of a sequential polymer composition, or as the acrylic polymer part of a u/a hybrid.

By an acrylic polymer herein is meant a homo- or copolymer derived from the addition polymerisation (using a free radical initiated process and usually in an aqueous medium), preferably by aqueous emulsion polymerisation, of a monomer composition comprising at least 40 weight % of one or more monomers of the formula:



where R^2 is H or methyl, and R^3 is optionally substituted alkyl of 1 to 20 carbon atoms (more preferably 1 to 8 carbon atoms) or cycloalkyl of 5 to 20 carbon atoms. Such monomers are referred to herein as acrylic monomers. More preferably, the monomer composition contains at least 50 weight % of acrylic monomer(s), and particularly at least 60 weight %. Examples of such acrylic monomers include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-propyl acrylate, n-propyl methacrylate, and hydroxyalkyl (meth)acrylates such as hydroxyethyl acrylate, hydroxyethylmethacrylate 2-hydroxypropyl methacrylate, and 2-hydroxypropyl acrylate. Preferred acrylic monomers include methyl methacrylate, n-butyl acrylate, n-butyl methacrylate and 2-ethylhexyl acrylate.

The monomer composition to form the acrylic polymer may of course include monomer(s) other than the acrylic monomers defined above and which is (are) copolymerised with one or more of such acrylic monomers. Examples of such monomers include 1,3-butadiene, isoprene, styrene, α -methyl styrene, divinyl benzene, acrylonitrile, methacrylonitrile, vinyl halides such as vinyl chloride vinyl esters such as vinyl acetate, vinyl propionate, vinyl laurate, and vinyl esters of versatic acid such as VeoVa 9 and VeoVa 10 (VeoVa is a trademark of Shell), heterocyclic vinyl compounds, alkyl esters of mono-olefinically unsaturated dicarboxylic acids (such as di-n-butyl maleate and di-n-butyl fumarate, and olefinically unsaturated monocarboxylic or dicarboxylic acids, such as acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, fumaric acid, maleic acid, and itaconic acid. Particularly preferred other monomers are selected from acrylic acid, methacrylic acid, styrene and acrylonitrile.

The polymerisation of the monomer composition to form an acrylic polymer will normally require the use of a free-radical-yielding initiator(s) to initiate the polymerisation. Suitable free-radical-yielding initiators include inorganic peroxides such as K, Na or ammonium persulphate, hydrogen peroxide, or percarbonates; organic peroxides, such as acyl peroxides including for example benzoyl peroxide, alkyl hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; dialkyl peroxides such as di-t-butyl

peroxide; peroxy esters such as t-butyl perbenzoate and the like; mixtures may also be used. The peroxy compounds are in some cases advantageously used in combination with suitable reducing agents (redox systems) such as Na or K pyrosulphite or bisulphite, and i-ascorbic acid. Azo compounds such as azoisobutyronitrile may also be used. Metal compounds such as Fe.EDTA (EDTA is ethylene diamine tetracetic acid) may also be usefully employed as part of a redox initiator system. An initiator system partitioning between the aqueous and organic phases, for example a combination of t-butyl hydroperoxide, iso-ascorbic acid and Fe.EDTA, may be of particular use. The amount of initiator or initiator system to use is conventional, for example within the range 0.05 to 6 wt % based on the total monomer(s) used.

An aqueous polymerisation to form acrylic polymer which is carried out in absence of polyurethane normally needs to be performed in the presence of a stabilising and/or dispersing material, and when making an aqueous latex of a acrylic polymer, a conventional emulsifying agent would need to be employed (e.g. anionic and/or nonionic emulsifiers such as Na salts of dialkylsulphosuccinates, Na salts of sulphated oils, Na salts of alkyl sulphonic acids, Na, K and ammonium alkyl sulphates such as sodium lauryl sulphate, C₂₂₋₂₄ fatty alcohols, ethoxylated fatty acids and/or fatty amides, and Na salts of fatty acids such as Na stearate and Na oleate; the amount used is usually 0.1 to 5% by weight on the weight based on the total olefinically unsaturated monomer(s) used). When incorporated using an in-situ process however (to form a u/a hybrid), a polyurethane polymer containing internal dispersing groups usually removes the requirement for the use of a separately added conventional emulsifying agent since the polyurethane itself acts as an effective dispersant for the polymerisation, although a conventional emulsifier can be still employed if desired.

A buffer material, such as sodium bicarbonate, is often employed in polymerisations to form acrylic polymers.

The Mw of an acrylic polymer employed in the invention dispersion is usually within the range of from 20,000 to 5,000,000 g/mole, more preferably 100,000 to 1,500,000 g/mole. (Molecular weights are determined herein using gel permeation chromatography using a polymer, e.g. styrene, of known molecular weight as a standard).

In the invention dispersion, it is preferred that the weight average particle diameter (Dw) (i.e. the particle size - since the particles are essentially spherical) of the polyurethane particles or u/a hybrid particles is within the range of from 20 to 200 nm, more preferably 30 to 150 nm, and Dw of the acrylic polymer particles is within the range of from 30 to 500 nm, more preferably from 45 to 250 nm and most preferably from 60 to 200 nm. Preferably, Dw of the acrylic polymers is larger than Dw of the polyurethane or u/a hybrid particles. (It is to be understood that Dw is applicable to, i.e. is the average of, bimodal or polymodal particle size distributions, as well as monomodal distributions).

The disposition of the defined acrylic and polyurethane polymers in the invention dispersion can be envisaged in several embodiments, the following being exemplary (but not limiting):

- 1) a blend of soft and hard acrylic polymers (separately prepared) may be in admixture with a polyurethane(s), or alternatively with a u/a hybrid in which the acrylic polymer part may be a single acrylic polymer (one Tg) which may be soft or hard or may be a combination of soft and hard acrylic polymers;
- 2) a soft acrylic polymer may be in admixture with a u/a hybrid which contains at least one hard acrylic polymer;
- 3) a hard acrylic polymer may be in admixture with a u/a hybrid which contains at least one soft acrylic polymer;
- 4) a sequentially polymerised combination of at least one hard acrylic polymer and at least one soft acrylic polymer (where the soft acrylic polymer is polymerised in the presence of the hard acrylic polymer, or vice versa) may be in admixture with a polyurethane(s), or alternatively with a u/a hybrid in which the acrylic part is a single acrylic polymer having a soft or hard Tg, or two or more acrylic polymers having differing Tg's (either of which may be soft or hard).

The invention dispersion, as discussed above, has an exceptionally advantageous combination of low MFFT and high hardness and good blocking properties. It is preferred that the MFFT of the invention dispersion is $\leq 25^{\circ}\text{C}$, more preferably $\leq 20^{\circ}\text{C}$ and most preferably $\leq 15^{\circ}\text{C}$. Being aqueous based the lower limit of MFFT for the invention dispersion will be the freezing point of the aqueous carrier phase. This will usually be about 0°C (perhaps slightly lower if there are any dissolved constituents, although not usually below -2°C). It is further most preferred that the invention dispersions are entirely solvent free.

The minimum film forming temperature (MFFT) of a dispersion as used herein is the temperature where the dispersion forms a smooth and crackfree coating or film using DIN 53787 and applied using a Sheen MFFT bar SS3000.

Films made from the invention dispersions preferably have a Koenig hardness of from 35 to 200 seconds.

Koenig hardness as used herein is a standard measure of hardness, being a determination of how the viscoelastic properties of a film formed from the dispersion slows down a swinging motion deforming the surface of the film, and is measured according to DIN 53157 using an Erichsen hardness equipment.

As is well known, the glass transition temperature of a polymer is the temperature at which it changes from a glassy brittle state to a plastic, rubbery state.

The solids content of an aqueous dispersion of the invention is usually within the range of from about 20 to 65 wt % on a total weight basis, more usually 30 to 55 wt %. Solids content can, if desired, be adjusted by adding water or removing water (e.g. by distillation or ultrafiltration).

The weight ratio of the polyurethane polymer(s) to the acrylic polymers (i.e. the total amount and wherever located) in the aqueous invention dispersion composition is preferably within the range of from 3/97 to 55/45, more preferably from 5/95 to 40/60 and most preferably from 10/90 to 30/70.

The aqueous dispersions of the invention may be used in various applications and for such purposes may be further optionally combined or formulated with other additives or components (to form compositions), such as defoamers, rheology control agents, thickeners, dispersing and stabilising agents (usually surfactants), wetting agents, fillers, extenders, fungicides, bacteriocides, anti-freeze agents, waxes and pigments.

The aqueous dispersions may for example be used, appropriately formulated if necessary, for the provision of films, polishes, varnishes, lacquers, paints, inks and adhesives. However, they are particularly useful and suitable for providing the basis of protective coatings for wooden substrates (e.g. wooden floors), and plastics, paper and metal substrates.

The dispersions (or compositions) once applied may be allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat.

The present invention is now further illustrated but in no way limited by reference to the following examples. Unless otherwise specified all parts, percentages, and ratios are on a weight basis. The prefix C before an example number denotes that it is comparative.

The glass transition temperatures of the polymers in the examples were calculated by means of the Fox equation. Thus the T_g , in degrees Kelvin, of a copolymer having "n" copolymerised comonomers is given by the weight fractions W of each comonomer type and the T_g 's of the homopolymers (in degrees Kelvin) derived from each comonomer according to the equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_n}{T_{gn}}$$

The calculated T_g in degrees Kelvin may be readily converted to °C.

General Procedure for Preparation and Testing of Multipolymer Dispersions

All polymerisations to form acrylic polymers were conducted in a 2 litre reaction vessel equipped with a stirrer, reflux condenser, thermometer and nitrogen purge. A thermostatted heating mantle was used to heat the reaction vessel. The ingredients for

the polymerisations were added as indicated in the specific examples below. At the end of the polymerisations all dispersions were pH adjusted to a pH of 7.5 - 8.0 using 12.5% aqueous ammonia solution.

The compositions of the polymers including the calculated Tg values from the Fox equation, are shown in Table 1.

For the examples, single hard and soft acrylic polymers were prepared, as was a simple blend of these polymers. Also prepared were the sequentially formed acrylic compositions of soft/hard and hard/soft acrylic polymers (soft/hard indicates that the hard acrylic polymer is formed in the presence of a first-formed soft acrylic polymer, and vice versa for a hard/soft acrylic polymer). The acrylic polymers (single polymer, simple blend or sequential) are then combined with a commercially available, solvent free, anionically stabilised, aqueous aliphatic polyurethane dispersion NeoRez R980 at varying levels. NeoRez R980 is available from Avecia BV and NeoRez is a registered Trade Mark. This polyurethane dispersion is in accordance with the polyurethane as defined in the invention dispersion.

Preparation of Acrylic Polymer Compositions (Simple Blends and Sequential) Synthesis of a hard acrylic polymer AP1.

| | | |
|----|--|------------|
| 20 | (A) Initial charge mixture | g |
| | Demineralised water | 781.40 |
| | Buffer - sodium bicarbonate (25% aqueous solution) | 2.06 |
| | Surfactant - sodium lauryl sulphate (30% aqueous solution) | 14.61 |
| 25 | (B) Pre-emulsified monomer mixture | |
| | Sodium lauryl sulphate (30% aqueous solution) | 44.08 |
| | Demineralised water | 211.25 |
| | Sodium bicarbonate (25% aqueous solution) | 5.94 |
| | Initiator - ammonium persulphate | 2.01 |
| 30 | Methacrylic acid | 21.92 |
| | n-Butyl methacrylate | 229.72 |
| | Methyl methacrylate | 625.14 |
| 35 | (C) Initial charge monomer mixture | 10% of (B) |

The initial charge mixture (A) was transferred to the reaction vessel and stirred under nitrogen purge. The heating mantle was turned on and at 50°C monomer initial charge (C) was charged. The temperature was taken to 90°C and the remaining pre-emulsified monomer feed was fed over 90 minutes. The temperature during this time was

maintained between 89-90°C. The resulting acrylic polymer latex was then cooled and filtered using 200 mesh filter cloth. The solids content of this latex was approximately 45% and its average particle diameter was 114 nm.

5 **Synthesis of a soft acrylic polymer AP2**

The recipe and procedure was identical to that used for making AP1, except that the monomers in the pre-emulsified mixture (B) were substituted as given below.

| | | |
|----|----------------------|--------|
| 10 | | g |
| | Methacrylic acid | 43.84 |
| | n-Butyl methacrylate | 505.03 |
| | Methyl methacrylate | 80.66 |
| | n-Butyl acrylate | 247.25 |

15

This acrylic polymer latex had a solids content of approximately 45% and an average particle diameter of 110nm.

20 **Synthesis of an acrylic polymer AP3 having the average composition of a 50/50 blend of AP1 and AP2**

The recipe and procedure was identical to that for making AP1, except that the pre-emulsified monomer mixture (B) was replaced as given below.

| | | |
|----|---|--------|
| | | g |
| 25 | Sodium lauryl sulphate (30% aqueous solution) | 35.15 |
| | Demineralised water | 211.88 |
| | Sodium bicarbonate (25% aqueous solution) | 5.96 |
| | Ammonium persulphate | 2.02 |
| | Methacrylic acid | 32.87 |
| 30 | n-Butyl methacrylate | 367.37 |
| | Methyl methacrylate | 352.90 |
| | n-Butyl acrylate | 123.63 |

35

This acrylic latex had a solids content of approximately 45% and an average particle diameter of 121nm.

Synthesis of a hard/soft sequential acrylic polymer composition AP4

| | g |
|--|---|
| (A-4) Initial charge mixture | same as in AP1 (A). |
| (B-4a) Pre-emulsified monomer mixture I | |
| 5 Sodium lauryl sulphate (30% aq solution) | 17.57 |
| Demineralised water | 103.42 |
| Sodium bicarbonate (25% aq solution) | 2.98 |
| Ammonium persulphate | 1.01 |
| Methacrylic acid | 10.96 |
| 10 n-Butyl methacrylate | 114.86 |
| Methyl methacrylate | 312.57 |
| (B-4b) Pre-emulsified monomer mixture II | |
| Sodium lauryl sulphate (30% aq solution) | 17.57 |
| 15 Demineralised water | 126.04 |
| Sodium bicarbonate (25% aq solution) | 2.98 |
| Ammonium persulphate | 1.01 |
| Methacrylic acid | 21.92 |
| n-Butyl methacrylate | 252.51 |
| 20 Methyl methacrylate | 40.33 |
| n-Butyl acrylate | 123.63 |
| (C-4) Initial charge monomer mixture | 10% of (B-4a). |
| 25 | <p>The initial charge mixture (A-4) was transferred to the reaction vessel and stirred under nitrogen purge. The heating mantle was turned on and at 50°C monomer initial charge (C-4) was added. The temperature was taken up to 90°C and the remaining pre-emulsified monomer feed I (B-4a) was fed over 90 minutes. The temperature was maintained between 88-90°C. Once the feed B-4a was completed, the pre-emulsified monomer mixture II (B-4b) was commenced and fed over a period of 90 minutes. The temperature was maintained at 88-90°C during the feed. The resulting hard/soft sequential acrylic polymer composition latex was then cooled and filtered using 200 mesh filter cloth. The solids content of the latex was approximately 45% and the average particle diameter was 108nm.</p> |
| 30 | |
| | |
| | |
| 35 | |

Synthesis of a soft/hard sequential acrylic polymer composition AP5

The recipe and procedure was identical to that used for making AP4, except that the order of the pre-emulsified monomer mixtures B-4a and B-4b was inverted. The

solids content of the resulting soft/hard acrylic polymer latex composition was 45% and the average particle diameter was 116 nm.

Table 1

| Acrylic polymer(s) | n-BMA (%) | n-BA (%) | MMA (%) | MAA (%) | Tg (°C) |
|--------------------|-----------|----------|---------|---------|---------|
| AP1 | 26.2 | - | 71.3 | 2.5 | 80.0 |
| AP2 | 57.6 | 28.2 | 9.2 | 5.0 | 5.0 |
| AP3 | 41.9 | 14.1 | 40.3 | 3.7 | 40.6 |
| AP4 | | | | | |
| hard pol. (50%) | 26.2 | - | 71.3 | 2.5 | 80.0 |
| soft pol. (50%) | 57.6 | 28.2 | 9.2 | 5.00 | 5.0 |
| AP5 | | | | | |
| soft pol. (50%) | 57.6 | 28.2 | 9.2 | 5.0 | 5.0 |
| hard pol. (50%) | 26.2 | - | 71.3 | 2.5 | 80.0 |

Preparation of a simple latex blend of hard and soft polymers AP6

A 1:1 mixture of the latices of AP1 and AP2 was formed by simple mixing.

Examples C1, C2, C3, 4, 5 and 6

Preparation of Aqueous Multipolymer Dispersions of acrylic and polyurethane polymers

The acrylic polymer latices AP1 to AP6 were blended with NeoRez R980 at levels up to 50 wt % in Examples C1, C2, C3, 4, 5 and 6, and MFFT measured at each level.

The results are shown in Table 2.

Table 2

| Example No | Acrylic used | MFFT (°C) with different levels of NeoRez R980 | | | | | |
|------------|--------------|--|------|-----|-----|-----|-----|
| | | 0%* | 10% | 20% | 30% | 40% | 50% |
| C1 | AP1 | > 90 | > 90 | 90 | 73 | 29 | < 0 |
| C2 | AP2 | 5 | < 0 | < 0 | < 0 | < 0 | < 0 |
| C3 | AP3 | 53 | 47 | 41 | 34 | < 0 | < 0 |
| 4 | AP4 | 27 | 13 | 8 | 3 | < 0 | < 0 |
| 5 | AP5 | 64 | 54 | 37 | 26 | 21 | < 0 |
| 6 | AP6 | 8 | 4 | 3 | < 0 | < 0 | < 0 |

*it will be appreciated that all dispersions at 0% of urethane are comparative.

The early blocking and hardness results of Examples C2, 4 and 6, using a level of 30% (wt % on dispersion) of NeoRez R980, are shown in Table 3.

5

Table 3

| Example No | Acrylic Used | MFFT (°C) | Blocking Resistance | Koenig Hardness (sec) |
|------------|--------------|-----------|---------------------|-----------------------|
| C2 | AP2 | < 5 | 3 | 22.9 |
| 4 | AP4 | < 5 | 5 | 58.6 |
| 6 | AP6 | < 5 | 5 | 44.3 |

Blocking Resistance

10 Films were cast on Leneta chart 2C, at 100µm wet film thickness. After flash off time of 5 minutes at room temperature the films were transferred to an oven at 60°C for 20 minutes. Blocking resistance was performed by placing the respective films face to face and placing a 3Kg/cm² weight at 50°C for 4 hours. After this test period the films were separated by hand and a rating (0 - 5) of the block resistance was given. 0 = poor separation and 5 = excellent separation.

15

Koenig Hardness

Films were cast on glass at 80µm wet film thickness at room temperature and allowed to stand for 30 minutes. The films were then transferred to an oven at 60°C and left for 16 hours. The hardness of the films were measured using an Erichsen hardness equipment.

Claims

1. Aqueous multipolymer dispersion which is substantially solvent-free and which comprises the following polymers:

- 5 (A) an acrylic polymer(s) having a Tg of less than 20°C;
(B) an acrylic polymer(s) having a Tg of at least 20°C;
wherein the Tg of the polymer(s) of (B) is at least 30°C higher than the Tg of the polymer(s) of (A), preferably at least 50°C;
(C) a polyurethane polymer(s) which is a chain-extended product formed from
10 reactants which comprise:
(1) an aqueous-dispersed isocyanate-terminated prepolymer having an acid value of ≤ 35 mg KOH/g of prepolymer (solids), preferably ≤ 30 mgKOH/g, and being formed from reactants which comprise:
(i) at least one organic polyisocyanate,
15 (ii) an organic isocyanate-reactive component comprising at least one polymeric polyol, and
(2) an active hydrogen chain-extending compound(s);
wherein said polyurethane polymer has less than 0.2 mmole per gram of olefinically unsaturated bonds.

20 2. Dispersion according to claim 1 wherein the Tg of the polymer(s) of (B) is at least 65°C higher than the Tg of the polymer(s) of (A).

25 3. Dispersion according to either claim 1 or claim 2 wherein the weight ratio of the polymer(s) of (A) to the polymer(s) of (B) is within the range of from 30/70 to 90/10, preferably from 40/60 to 85/15, more preferably 45/55 to 80/20.

30 4. Dispersion according to any one of the preceding claims wherein the polyurethane polymer(s) of (C) by itself is film forming at ambient temperature, the weight ratio of the polymer(s) of (A) to the polymer(s) of (B) is within the range of from 30/70 to up to 50/50, and the combined amount of the film forming polyurethane polymer(s) of (C) and the polymer(s) of (A) corresponds to at least 45 weight % of the total amount of the polymers of (A), (B) and (C), more preferably at least 50 weight %.

35 5. Dispersion according to any one of claims 1 to 3 wherein the polyurethane polymer(s) of (C) by itself is non film forming at ambient temperature, the weight ratio of the polymer(s) of (A) to the polymer(s) of (B) is within the range of from more than 50/50 to 90/100, and the combined amount of the non film forming polyurethane polymer(s) of

(C) and the polymer(s) of (B) corresponds to less than 55 weight % of the total weight of the polymers of (A), (B) and (C), more preferably less than 50 weight %.

5 6. Dispersion according to any one of the preceding claims wherein the acrylic polymers of (A) and (B) are present at least as a simple blend of the separately prepared polymers.

10 7. Dispersion according to any one of the preceding claims wherein the acrylic polymers of (A) and (B) are present at least as a sequentially formed composition of the polymers.

15 8. Dispersion according to any one of the preceding claims wherein the acrylic polymer(s) of (A) or (B) is present at least as part of a polyurethane/acrylic polymer hybrid.

9. Dispersion according to claim 8 wherein the weight ratio of polyurethane polymer to acrylic polymer(s) in the polymer hybrid is within the range of from 5/95 to 99/1, preferably from 15/85 to 90/10, more preferably from 30/70 to 80/20.

20 10. Dispersion according to any one of the preceding claims wherein the weight ratio of the acrylic polymers (the total amount wherever located) to the polyurethane polymer is within the range of from 3/97 to 55/45, preferably from 5/95 to 40/60, more preferably from 10/90 to 30/70.

25 11. Dispersion according to any one of the preceding claims wherein the chain-extending compound(s) used for the polyurethane is hydrazine or a di- or triamine of number average molecular weight below 300.

30 12. Dispersion according to any one of the preceding claims wherein the polyurethane polymer(s) has less than 0.1 mmole per gram, more preferably 0 mmole per gram, of olefinically unsaturated bonds.

35 13. Dispersion according to any one of the preceding claims wherein the polyurethane is self-water-dispersible and has internal dispersing groups selected from one or more of anionic, cationic and nonionic groups.

14. Dispersion according to any one of the preceding claims wherein the weight average molecular weight of the polyurethane is at least 10,000, preferably at least 25,000.

15. Dispersion according to any one of the preceding claims wherein the weight average particle diameter of the particles of the polyurethane(s) or urethane/acrylic hybrid is within the range of from 20 to 200 nm, more preferably from 30 to 150 nm.

5

16. Dispersion according to any one of the preceding claims wherein the weight average particle diameter of the particle of the acrylic polymer(s) is within the range of from 30 to 500 nm, more preferably from 45 to 250 nm.

10

17. Dispersion according to any one of the preceding claims having MFFT below 25°C, more preferably 20°C.

18. Dispersion according to any one of the preceding claims, said dispersion being entirely solvent-free.

15

19. Aqueous coating composition which is substantially solvent-free and comprises an aqueous multipolymer dispersion according to any one of claims 1 to 18.

20

20. Method of coating a substrate using an aqueous dispersion according to any one of claims 1 to 18 or a coating composition according to claim 19.

21. Coating obtainable or derived from an aqueous dispersion according to any one of claims 1 to 18 or a coating composition according to claim 19.

25

22. Substrate having a coating according to claim 21.

23. Dispersion substantially as described in examples 4, 5 and 6.



INVESTOR IN PEOPLE

Application No: GB 0111154.1
Claims searched: 1-23

24

Examiner: Dr Albert Mthupha
Date of search: 30 August 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.S): C3M (MXAW)
Int CI (Ed.7): C09D (133/08, 133/10, 133/12, 175/04, 175/12)
Other: ONLINE : CAS ONLINE, EPODOC, JAPIO, WPI.

Documents considered to be relevant:

| Category | Identity of document and relevant passage | Relevant to claims |
|----------|---|--------------------|
| A | GB 2298208 A CRAY VALLEY, see whole document. | |
| A | EP 0829757 A2 EASTMAN KODAK, note Examples. | |
| A | EP0601219 A1 DU PONT, see whole document. | |

| | | | |
|---|---|---|--|
| X | Document indicating lack of novelty or inventive step | A | Document indicating technological background and or state of the art. |
| Y | Document indicating lack of inventive step if combined with one or more other documents of same category. | P | Document published on or after the declared priority date but before the filing date of this invention. |
| & | Member of the same patent family | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |